ternal reference. Thermogravimetric analyses (TGAs) of polymer powders (about 5 mg) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of 10 °C/min with an air flow of 75 ml/min was used, the runs being conducted from room temperature to 800 °C. Conductivity measurements were carried out on a four-point probe connected to a Keithley 220 programmable current source and a 2000 multimeter system. Scanning electron micrographs were obtained on a JEOL JSM-35CF scanning electron-microscope. GPC analyses were carried out using a Perkin Elmer Model 200 HPLC system with Pheno-gel MXL and MXM columns (300 mm × 4.6 mm I.D.) calibrated using poly-styrene standards and THF as eluent. Electrochemical polymerization and cyclic voltammetry in 2 M HCl were performed with an EG&G Model 273 potentiostat/galvanostat controlled by the EG&G M270 electrochemical software. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCA/SIMLAB MKII spectrometer equipped with a Mg K_α radiation source. All core-level spectra were corrected for surface charging by reference to the designated C(1s) binding energy at 285.0 eV. Spectra deconvolutions were carried out using a Gaussian component with the same full width at half maximum (FWHM) for each component in a particular spectrum.

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Does the Self-Assembled Coating of Magnetic Nanoparticles Cover Individual Particles or Agglomerates?

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The formation of monolayers of surfactant molecules on the surfaces of nanoparticles is one example of the general phenomenon of self-assembly (SA). In nature, self-assembly results in supermolecular hierarchical organizations of interlocking components that may provide very complex systems. Numerous publications have reported on the synthesis and characterization of SA monolayer coatings of various organic surfactants on flat polished surfaces of metal or metal oxides.[1] Fewer publications have described the synthesis and characterization of SA coatings on metal or metal oxide particles.[2–5]

The study of coatings on the surface of ultrafine powders is of great interest, because the surfactant acts as a stabilizer and is believed to prevent agglomeration.[6–13] The usage of coated nanoparticles includes catalysis, biological cell separation, raw material recovery, drug delivery and anti-corrosion protection. The coatings of magnetic nanoparticles are of special interest because of their important technological applications in electronics, solar energy transformation, magnetic recording, magnetic fluids, and magnetic refrigeration systems, etc.

Coating the surface changes the intrinsic physico-chemical properties of small particles. In a few studies, the ratio of the amount of surfactant to that of the metallic substrate was varied, and the average size of dispersed substance was determined as a function of this ratio.[6–8,10–12,14,15] In all of the above-mentioned work, the general trend has been that the higher the amount of surfactant, the smaller the resulting particle. Nanoparticles of both non-magnetic metals, such as gold[6,7,16–18] or copper,[12] and magnetic metals[8,10,19–21] were deliberately isolated, so that interaction between separated particles could be neglected, resulting in suppression of agglomeration.

Amorphous iron nanoparticles can be coated with organic molecules such as octadecyltrichlorosilane (OTS) or sodium dodecylsulfate (SDS), as has recently been demonstrated.[3,22] The study was extended, and long chain

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thiols[23] and alcohols[24] were added to the previous molecules. Amorphous iron oxide nanometer-sized particles were coated with octadecanethiol, as well.[25]

As is pointed out above, SA coatings change the properties of the whole material. In particular, they influence its magnetic properties. It is known that a small magnetic particle becomes monodomain below some critical size due to the interplay between the energy of dipole fields and domain wall creation.[26–38] Consequently, it has large spontaneous magnetization, typically of the order of many thousands Bohr magneton. In the absence of interactions between magnetically isotropic particles such assembly would behave as a paramagnetic material, described by a standard Langevin function. This phenomenon is called "superparamagnetism". In the presence of magnetic anisotropy and interactions, which are always present in magnetic particles, the magnetic behavior changes. For example, Langevin function becomes a poor approximation of $M(H)$ curves and zero-field cooled (ZFC) $M(T)$ curves do not coincide with field cooled (FC) curves below some temperature called the blocking temperature T_B. This magnetic blocking appears because below T_B thermal energy is not enough to overcome the energy of magnetic anisotropy and magnetic interactions. The general trend is that T_B shifts towards higher temperatures when the strength of interactions between particles increases. The same is true for an increase of the magnetic anisotropy.[35]

As in all previous reports related to the sonochemical synthesis of amorphous nanopowders,[32,39–44] the agglomeration of magnetic particles has been observed, making it difficult to detect the individual 2–3 nm-sized particles. The existence of such small magnetic nanoparticles is deduced from the superparamagnetic behavior that has been detected for all sonochemically prepared nanoparticles and is known to be connected with 2–5 nm size particles. Moreover, magnetic nanoparticles tend to agglomerate due to magnetic interaction during the process of SA coating. However, capping of individual magnetic nanoparticles by the molecules of dispersant has been observed.[45] We have reported recently that SAM coating affects the morphology and, subsequently, the magnetic behavior of coated nanometer-size material.[46]

In the present work we use magnetic measurements of the blocking temperature to analyze SA coatings. The argument is as follows: if a surfactant covers each individual nanoparticle, the inter-particle separation increases, thus reducing the magnetic dipole–dipole interaction. This must lead to a significant shift in T_B for coated particles. Moreover, increasing the length of the alkylthiol chain in a series of thiol-coated particles must push T_B further down. Indeed, surfactant changes surface magnetic anisotropy as well. Fortunately, it leads to an increase of the surface spins disorientation (spin canting[34,35]) resulting in the decrease of the magnetic moment and thus T_B also decreases. Therefore, if the SA fully coats each individual particle we should observe a progressive shift of T_B to lower temperatures

with the increase of the alkanethiol chain length. If, however, the coating is carried out on the agglomerate surface, there should be almost no change in T_B when the alkyl chain length is increased.

The magnetization measurements were conducted on samples coated by thiols of different chain length with equal molar ratio of thiol/oxide (3/1). Results of room temperature measurements (VSM) (see Fig. 1) show decrease in magnetization with increase of the alkanethiol chain length. At the same time, the surface area of measured samples has no significant change. This can be explained by the increasing amount of non-magnetic substance (the number of −CH_2 units in the chain of organic molecules) per each nanoparticle of iron oxide.
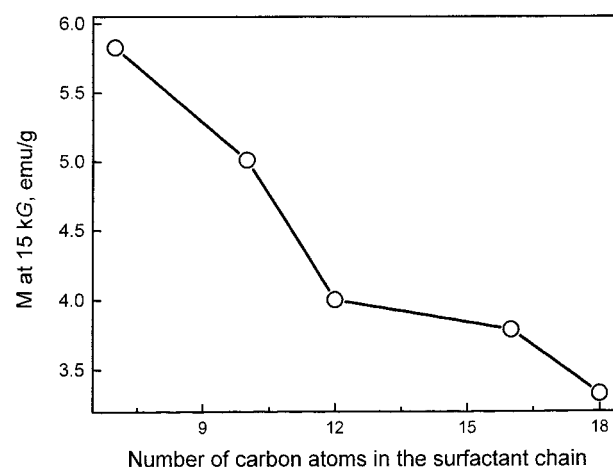

Fig. 1. The magnetization vs. the alkylthiol chain length.

The magnetization vs. temperature measurements (SQUID, superconducting quantum interference device) were carried out for non-coated amorphous iron oxide and for the samples prepared with equal molar ratio of the alkanethiol/oxide (3/1). These measurements resulted in a change of T_B for non-coated amorphous iron oxide compared with that of an octadecanethiol-coated sample (see Fig. 2). On the other hand, the T_B for samples coated with various alkanethiols, hardly changed with increase of the carbon chain length, whereas the magnetization value decreased (see Table 1). This may indicate that the average distance between the magnetic nanoparticles does not change. We related this data to the fact that the SA coating process of amorphous iron oxide by the molecules of thiols takes place on the surface of the oxide aggregates and not on the surfaces of separated nano-sized oxide particles.

We calculate the approximate size of covered unit using the measured values of surface area, density, and percentage of sulfur. The latter has been deduced from elemental analysis (see Table 2). Assuming that one molecule of surfactant occupies 20 Å^2,[47] we estimate the diameter of a full-coated agglomerate of about 60–80 nm. This number correlates well with that observed directly by TEM (see Fig. 3). Using simple calculations one can see, that in the
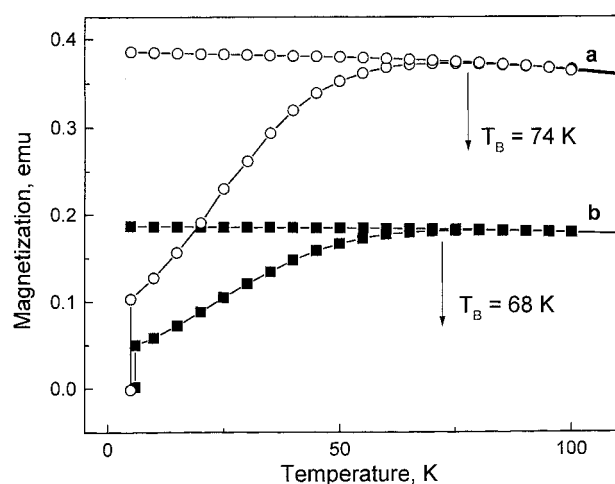
Fig. 2. The ZFC and FC curves for (a) non-coated and (b)octadecanethiol-coated amorphous iron oxide.

Table 1. The magnetization and blocking temperature for alkanethiol-coated amorphous iron oxide nanoparticles.

Surfactant used	T_B, K	Shift$_{calc}$ of T_B, K
Noncoated iron oxide	73	-
Heptanethiol	69	3.4
Decanethiol	69	3.9
Dodecanethiol	68	5.1
Hexadecanethiol	68	6.1
Octadecanethiol	68	6.8

Table 2. The parameters of amorphous iron oxide nanoparticles coated with the molecules of various chain length alkanethiols

Surfactant used	Surface area, m²/g	Sulfur, % (weight)
Noncoated iron oxide	168	-
Heptanethiol	107	3.35
Decanethiol	106	3.25
Dodecanethiol	104	3.2
Hexadecanethiol	103	3.1
Octadecanethiol	103	3.08

case of full monolayer coverage of all individual iron oxide nanoparticles with mean particle size of 2-3 nm by the molecules of alkanethiols, we should detect a *much larger* percentage of sulfur component than that measured. Since the sulfur content is very low, we can conclude, that the SAM coating took place on the surface of already agglomerated nanoparticles. The calculated diameter of agglomerates also correlates well with the estimated shift in T_B. This estimation is performed assuming a dipolar character of inter-
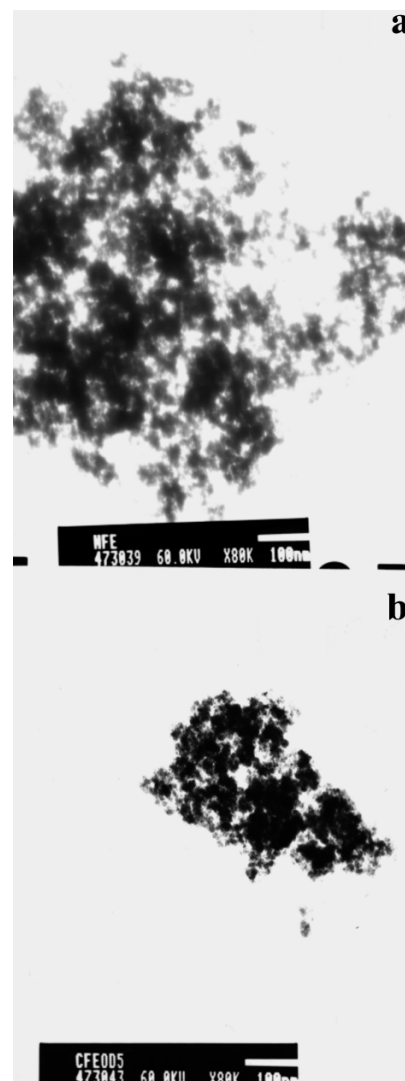

Fig. 3. TEM images of (a) non-coated and (b)octadecanethiol-coated amorphous iron oxide.

particle interactions proportional to $1/r^3$. For $d = 60$ nm and alkylthiol chain length of about 1 nm (for octadecanethiol), this shift is 6.8 K, that is, very close to the observed 6.0 K (see Table 1). If the coating took place on the individual particles of $d = 6$ nm, the shift would be 27.4 K.

Using measurements of samples with different lengths of the surfactant molecule we have concluded for the first time that the SAM coating takes place on the surface of the agglomerates, rather than on the surface of separate nanoparticles. This result is confirmed by elemental analysis, surface area and magnetic measurements.

Experimental

Amorphous iron oxide nanoparticles were prepared and SA coated with the molecules of thiols according the sonochemical method described elsewhere [25,43,44,46]. The amorphous nature of the particles was previously demonstrated by X-ray diffraction as well as by electron-diffraction patterns [43,44]. Briefly, a 1 M solution of Fe(CO)$_5$ in dry decaline was sono-

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chemically irradiated at 0 °C under ambient air atmosphere for 3 h. First, the powder obtained was centrifuged, washed repeatedly with dry pentane (6–7 times, 8500 r.p.m.), and dried in vacuum at room temperature for 3 h. Then, in order to remove organic residue, material was annealed in vacuum at 140–150 °C for 3 h. The material obtained was accumulated from 2–3 sonications and the total amount of Fe_2O_3 was mixed to ensure the reliability of the results. In the next step, nano-sized amorphous iron oxide was exposed to ethanolic solutions of alkanethiols with different alkyl chain, namely, heptanethiol, decanethiol, dodecanethiol, and hexadecanethiol. Probes with different mole ratio of alkanethiol/iron oxide in the coating solution were prepared this way, and then were agitated for 3 h at room temperature. The coated particles were centrifuged, washed repeatedly in ethanol (8–12 times, 8500 r.p.m.) in normal air atmosphere, and dried in vacuum for 3 h at room temperature. Dried away particles were subjected to further characterization.

The coated amorphous particles were exposed to further analysis, which included FT-IR, thermogravimetric analysis and differential scanning calorimetry, surface area measurements, TEM study, and magnetization measurements. These measurements were carried out for each molar ratio of the alkanethiol/Fe_2O_3 and for each length of thiol chain, respectively.

Surface area measurements were performed with Micromeritics surface area analyzer (Gemini 2375 system). These measurements were conducted applying the BET method, using nitrogen as the absorbate. Samples (≈30 mg) were degassed at 75 °C for 5 h and then placed into the surface area analyzer.

Magnetic measurements at room temperature were conducted on the Oxford Instrument vibrating sample magnetometer (VSM). 20–25 mg of iron oxide nanoparticles were inserted into the gelatin capsule and plugged with cotton to prevent dispersal of powder. Temperature resolved magnetic measurements were conducted using a Quantum Design MPMS SQUID magnetometer. The blocking temperature was measured recording ZFC (zero-field cooled measurements) and FC (field cooled measurements) M vs. T curves at the external magnetic field of 500 Gauss. Specifically, measurements were performed by cooling a sample in zero field down to 5 K whence a magnetic field of 500 G was applied. After that, the sample was slowly warmed up to a high temperature (typically 300 K) in steps of a few K with stabilization at each temperature and subsequent measurement of the magnetic moment (ZFC). Then, without turning magnetic field off, the sample was cooled down to 5 K with measurements of magnetic moment at each intermediate temperature (FC). The temperature at which the two curves, ZFC and FC, merge is traditionally called the blocking temperature T_B. This pretty-well defined temperature is the important parameter characterizing the magnetic behavior of fine particles.

Elemental analysis was carried out on Eager 200 CE Instruments EA 1110 Elemental Analyzer. The values of percent carbon (%C) and sulfur (%S) of the coatings are an average of measurements performed on at least three samples of each coating and have a maximum error of around ±5 %.

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Self-Assembling Functional Molecules in Mesoporous Silicate Materials: Optical Properties and Mesophase of Dye-Doped M41S

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Mesoporous materials invented by scientists of the Mobil Corporation have attracted considerable interest since the first announcement in 1992.[1–4] The formation mechanism of mesoporous materials designated as M41S has been

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